ADVANCED CONCEPTS IN NANOTEXTURING OF SOLID SURFACES FOR COMPOSITE APPLICATIONS

E.J. Robinette*, A.A. Bujanda, J.D. Demaree, R.E. Jensen, S.H. McKnight
Materials Division
Weapons and Materials Research Directorate
Army Research Laboratory
Aberdeen Proving Ground, MD 21005

ABSTRACT

Nanotexturing of glass fibers has shown the potential to improve impact properties of glass reinforced composites. Previous work by Army researches determined that modifying fiber surfaces using a mixture of silane coupling agents that were both reactive and non-reactive towards the matrix phase, in conjunction with nanoscale colloidal silica, yielded a simultaneously high strength and tough composite. The focus of this work was to ascertain which factors of the silane and silica treatments were most influential in controlling the silica deposition on solid surfaces. The basis of the silane chemistry involves controlling the number of amine-functional groups on the fiber surface. Propyltrimethoxylsilane (PTMO) and aminopropyl-trimethoxysilane (APS) are silanes that contain a propyl group and a primary amine, respectively. By varying the ratio of these silanes in solution, the concentration of amine groups on the fiber surface can be controlled. The amine groups on the fiber surface act as potential sites for epoxy-amine reactions. Two routes were chosen for affixing silica to the surface using the amine groups. In the first route, a reverse silane reaction is carried out; where the epoxy groups of a non-hydrolyzed glycidylpropyltrimethoxysilane (GPS) react with surface amine groups. Upon hydrolysis, the methoxy groups of the silane are converted to hydroxyl groups that undergo a condensation reaction with the silica. The second route for silica deposition involves the functionalization of the silica. In a separate step, hydrolyzed GPS is reacted with the silica to yield epoxy-functional silica. The epoxy groups on the silica can react with the amine groups on the glass surface.

1. INTRODUCTION

Silane chemistry has been extensively used to tailor performance of glass-reinforced polymer matrix composites [Plueddeman, 1991]. Silane coupling agents can be chosen to improve the adhesion of the fibers with a polymer matrix for improvements in structural properties or conversely, be selected to have poor adhesion with the matrix for improved impact properties [Hirai, 1998]. Previous work by Army researchers showed that the impact energy absorption capabilities of fiber-glass reinforced composites can be increased without sacrificing structural integrity through the novel use of nanotextured surface treatments [Jensen and McKnight, 2006]. Through use of a binary coupling agent, they designed fiber-matrix interfaces with the intention to adhere at low strain rates for structural integrity and fail at high strain rates to improve impact energy through energy dissipation from fiber-matrix pull-out. Furthermore, they developed a co-deposition technique in which nanoscale colloidal silica was attached to the fiber surface for enhances frictional energy dissipation.

The current work presented here builds upon the work first accomplished by Jensen and McKnight. Our goal is to determine which aspects of silane treatment and silica deposition can be tailored for highly controlled polymer-solid interfaces. Additionally, we would like to assess how silica surface coverage can be modified to enhance any surface nanotexturing effects.

2. EXPERIMENTAL

2.1 Materials

Silicon wafers (p-doped 100 orientation, Silicon Quest International, Inc.) were used as model surfaces. The silanes used in this work included 3-aminopropyl-trimethoxysilane (APS) (Aldrich), 3-glycidoxypropyl-trimethoxysilane (GPS) (Aldrich), and propyltrimethoxy-silane (PTMO) (Aldrich). Ludox TMA (Aldrich) was the silica used in this work. The 22 nm particles are suspended at 34 wt.% in deionized water.

2.2 Sample Preparation

Prior to use, all organic matter was removed from the surface of the silicon wafers using a piranha etch, which comprised of a 3:1 H_2SO_4:H_2O_2 solution. Wafers were exposed until activity on the wafer surface had ceased. After etching, the wafers were triple rinsed in ultra-pure water and dried in an N_2 stream. Cleaned wafers were stored in a nitrogen environment until use.

Silane treatments involving various ratios of APS to PTMO were used to control the density of amine groups on the wafer surface. A 1 wt.% concentration of APS and PTMO was added to a 90/10 (v/v) ethanol/water solution for hydrolysis. For PTMO hydrolysis, acetic acid was added to the solution to achieve a pH of 4.5 and initiate acid-catalyzed hydrolysis. Each solution was given one

		Form Approved OMB No. 0704-0188
	Report Documentation Page	

1. REPORT DATE **01 NOV 2006**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**
4. TITLE AND SUBTITLE **Advanced Concepts In Nanotexturing Of Solid Surfaces For Composite Applications**		5a. CONTRACT NUMBER
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)		5d. PROJECT NUMBER
		5e. TASK NUMBER
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Materials Division Weapons and Materials Research Directorate Army Research Laboratory Aberdeen Proving Ground, MD 21005**		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release, distribution unlimited**		
13. SUPPLEMENTARY NOTES **See also ADM002075., The original document contains color images.**		
14. ABSTRACT		
15. SUBJECT TERMS		

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT **UU**	18. NUMBER OF PAGES **8**	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**			

hour for hydrolysis. To achieve desired APS:PTMO ratios, specific amounts of the APS and PTMO solutions were mixed for five minutes. Each wafer was dipped in the mixed solutions for one minute. Next, the wafers were dried in an N_2 stream and heated to 100ºC for one hour to allow full condensation of the silanols and to promote crosslinking. After APS:PTMO treatment, the wafers were stored in a nitrogen environment to limit moisture uptake from the atmosphere.

The APS:PTMO silane treatments resulted in surfaces containing various concentrations of amine, or NH_2, groups. In one silica deposition route, the amine sites were reacted to GPS through an epoxy-amine reaction. A solution comprising 1 wt.% GPS in methanol was heated to 60ºC. Methanol was used as the solvent to eliminate the potential for silane hydrolysis. The aminated wafers were dipped in solution for one minute and dried in an N_2 stream. The samples were heated to 100ºC for further drying and subsequently stored in a nitrogen environment. The next treatment allowed for the bonding of silica on the wafer surface. Silica was added to a 90/10 (v/v) ethanol/water solution with a pH of 4.5 (acetic acid) at various concentrations. The solution was mixed for five minutes at room temperature. Next, the GPS-treated wafers were dipped in the silica solutions for one minute. After dipping, the wafers were dried in an N_2 stream and heated to 100ºC for one hour. Samples were then stored in a nitrogen environment until testing.

A second silica deposition route required the functionalization of the silica nanoparticles with epoxy groups. A concentration of 1 wt.% GPS was acid-hydrolyzed (pH of 4.5 with acetic acid) in a 90/10 (v/v) ethanol/water solution for one hour. The solution was heated to 65-70ºC under agitation. The silica (in a 34 wt.% deionized water solution) was slowly pipetted into the GPS solution. After all silica was added, the reaction was given one hour for reaction at 65-70ºC. Next, aminated wafers were dipped in this solution (at 60º) for one minute to allow for silica bonding to the wafer. After dipping, the wafers were dried in an N_2 stream, heated to 100ºC for one hour, and stored in a nitrogen environment.

2.3 Rutherford Backscattering Spectrometry (RBS)

RBS techniques were used to determine the thickness of silane and silica layers on the wafers. All measurements were performed using a 1.2 MeV He^+ ion beam from a National Electrostatics 5SDH-2 tandem positive ion accelerator. The backscattering angle was 170 degrees, and the solid angle of the surface barrier detector was approximately 4 millisteradians. All spectra were fit and interpreted using the program RUMP (Doolittle, 1986). The areal densities of the coatings measured by RBS were converted to physical

thicknesses assuming a typical density for the film studied (2.65 g/cm^3 for silica, 2.2 g/cm^3 for polysiloxane).

2.4 X-Ray Photoelectron Spectroscopy

A Kratos Ultra X-ray photoelectron spectroscopy (XPS) system, equipped with a hemispherical analyzer, was used to characterize the surface composition of the silane-treated silicon wafers. A 140 W monochromatic Al Kα (1486.7eV) beam irradiated a 1 mm x 0.5 mm analyzed area. All spectra were taken at a 2 x 10-9 torr base vacuum environment or lower. Survey and elemental high resolution scans for C_{1s}, O_{1s}, N_{1s}, and Si2p were taken at a pass energy of 80 eV and 20 eV, respectively. The photoemission spectra allow quantitative (surface concentrations) and qualitative (functional group identification) information to be obtained. A hybrid electrostatic and magnetic lens column with an integral coaxial charge neutralizer was employed to maintain uniform surface charge for the exact spot under examination. Kratos' VISION software was utilized for all data analysis (linear background subtraction, curve fitting, peak integration, charge compensation).

2.5 Contact Angle Measurements

Water contact angle measurements were measured using a static contact angle set up that was based on the sessile drop method. Contact angles were recorded using a goniometer equipped with a CCD camera and an image capture program employing LabView software. Contact angles were measured using HPLC grade water by defining a circle about the drop, and recording the tangent angle formed at the substrate surface.

2.6 Field Emission Scanning Electron Microscopy (FESEM) and Imaging Software

Differences in silica-treated silicon surfaces were observed using scanning electron microscopy (SEM). A field emission scanning electron microscope (Hitachi, model S4700) was used in secondary electron mode, using an upper and lower detector mix. The magnification ranged from 2500x up to 100,000x and the working distance varied from 3 mm to 9 mm. Accelerating voltage could not be greater than 3 keV as significant charging on the substrate surface was observed. Several areas on each sample were investigated in order to discern the uniformity of the untreated and treated surfaces.

Surface coverage of the silica nanoparticles were quantified using (Image J, National Institute of Health) software. The FESEM images were uploaded into this software and the threshold was adjusted to most accurately depict the original image, as shown in Fig.1. The software calculates the coverage by counting the number of white and black pixels. All reported values of surface coverage were taken from an average of at least four images.
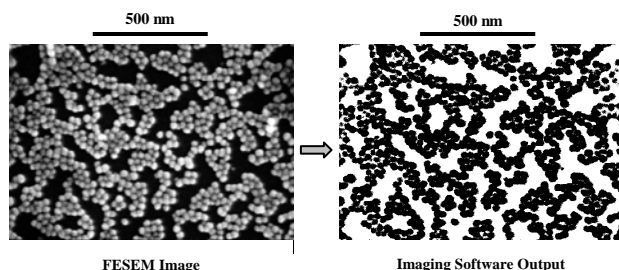
Fig.1. FESEM images are converted to black and white images using imaging software to calculate the surface coverage of silica particles.

2.7 Atomic Force Microscopy (AFM)

The surface roughness of the silane and silica treated silicon wafers were measured using a Digital Instruments Dimension 3100 AFM. To measure such small features as the nanosilica, Supersharp silicon tips (SSS-NCHR, NanoScience) were purchased. The RMS and RA roughness was measured across 1 μm scans in tapping mode at a scan rate of 1 Hz and 512 lines of resolution. All reported roughness values were taken as averages from three different scans on the wafer surface.

3. RESULTS AND DISCUSSION

The focus of this work was to control the surface coverage, and hence surface roughness, of silica particles reacted to a glass surface. All of these experiments were performed on model silicon wafer substrates to more precisely control the surface chemistry. The following section addresses several aspects of silane/silica chemistry. The first few sections cover details about the silane chemistry, the thickness of the silane layers, and the control of amine receptor groups. The subsequent sections discuss how parameters such as receptor group density, silica concentration in solution, and the functionalization of the silica particles influences areal surface coverage of the silica, particle agglomeration, and surface roughness of the wafers.

3.1 Silane Chemistry

Silane treatments typically involved three steps: hydrolysis, condensation, and crosslinking. Fig. 2 shows a schematic representation of these processes as they pertain to the silanes used in this work. During hydrolysis, alkoxy groups bonded to the silicon are converted to hydroxyl groups, thus creating organofunctional silanols. Hydrolysis occurs in both acidic and basic environments. PTMO is acid-hydrolyzed in this work. APS contains a polar NH_2 end group that inherently creates a basic environment for self-hydrolysis in ethanol-water solutions.

Although hydrolysis and condensation occurs simulateneously, the majority of condensation occurs

after most of the alkoxy groups have been converted to hydroxyl groups [Plueddeman, 1991]. During condensation, silanol groups can react with other silanols or with the silicon wafer surface that also contains hydroxyl groups. Since the silanes contain three reactive hydroxyl groups, the polysiloxane layer can crosslink and grow to a substantial thickness. After adequate reaction time, the silicon substrates are heated to further perpetuate crosslinking and remove water from the system.

Silane treatments can lead to substantially thick coupling layers. In glass-fiber applications, the presence of a thick coupling agent interphase can strongly influence material properties. In this work, we wanted to verify the thickness of the polysiloxane layer under the treatment conditions discussed in Section 2.2. RBS is a useful technique to determine chemical composition of a material, the depth distribution of elements near a surface, or the thickness of thin films. Fig. 3 shows an RBS plot for a silicon wafer which has been treated with APS and GPS. The most prominent feature in the spectrum is the "silicon edge", corresponding to the energy of backscattered 1.2 MeV He^+ ions from the silicon substrate. When the substrate is covered with a layer of coupling agent, the incident He^+ ions lose small amounts of energy as they traverse the layer, both on the way to the silicon substrate and again after the backscattering event. This energy loss results in a lower energy for the silicon edge; assuming one knows the composition and density of the layer, this energy loss can be converted to the physical thickness of the coupling agent layer. In the case of Fig. 3, the total polysiloxane layer was measured to be approximately 10 nm thick.
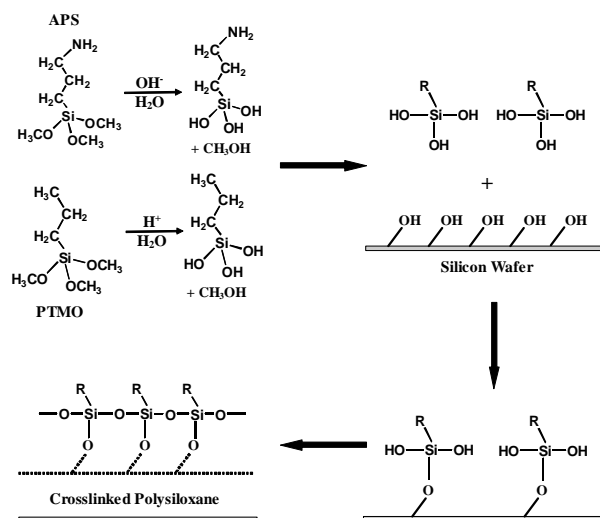

Fig. 2. Each silane, APS and PTMO, is hydrolyzed to form a silanol group. Silanol groups can then condense on the surface of a silicon wafer. Once bonded to the surface, further silanol condensation and crosslinking occurs to form a crosslinked polysiloxane interphase at the glass surface.
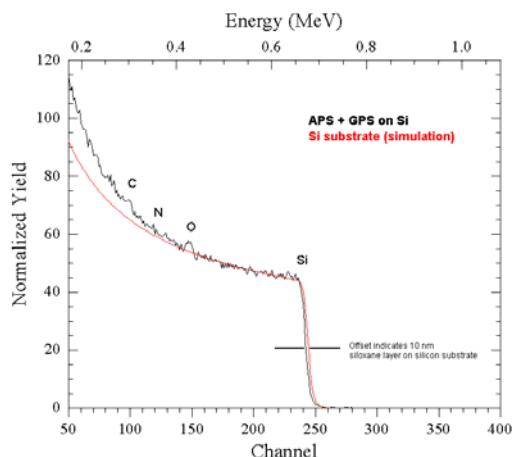
3

Fig 3. 1.2 MeV He$^+$ RBS spectrum of silicon wafer treated with polysiloxane, indicating a 10 nm coupling agent layer thickness.

3.2 Receptor Group Density

A combination of silanes can be used to design various surface chemistries of glass surfaces. In this work, a combination of both reactive (APS) and non-reactive silanes (PTMO) are used to control the density of amine receptor groups on the glass surface. Subsequent sections will address the importance of receptor group density on controlling the deposition of silica nanoparticles.

In order to control amine surface concentration, we combined various ratios of APS and PTMO during silanol condensation onto the silicon surface. Fig. 4 depicts a theoretical silicon surface after a silane treatment containing an APS:PTMO ratio of 3:2. This representation assumes the hydrolysis/condensation behavior for both silanes is the same and that no side reactions occur with the amine groups. Also, the arrangement of NH$_2$ groups on the surface will be random.
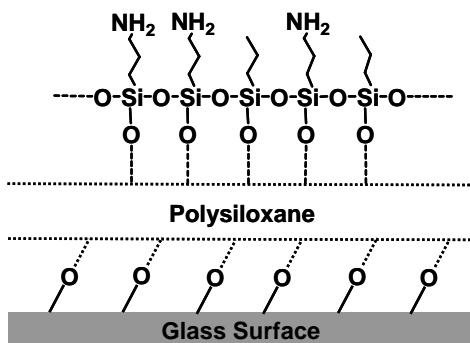

Fig 4. Ideal representation of a surface treated with 3 APS units to every 2 PTMO units.

XPS analysis was used to determine the exact concentration of surface amine groups. Fig. 5 relates surface amine content to the amount of APS present during silane condensation. The dotted line indicates the theoretical amine concentration calculated from the stoichiometry of the system. From Fig. 5, it appears the receptor group density is generally higher than what was calculated theoretically. An explanation for this behavior could be the difference in hydrolysis of the two silanes. The rate of self-hydrolysis for APS may have been slower than the acid-catalyzed hydrolysis of the PTMO. Therefore, a greater number of methoxy groups would be converted to hydroxyl groups for PTMO. If so, PTMO would react to the silicon surface at a faster rate than APS. Since APS condenses later than the PTMO, there would be more amine groups further from the silicon wafer surface. Future methods will be employed to determine this behavior. First, IR techniques can be used to determine the rate of hydrolysis for each silane. Next, angle resolve XPS can measure the amine concentration at different distances from the silicon wafer surface.
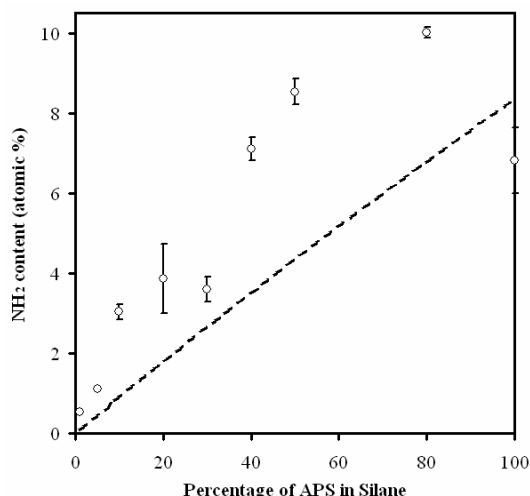

Fig. 5. XPS plot showing the amine concentration as a percentage of APS in the binary APS/PTMO silane.

Contact angle measurements are very sensitive to the surface energy of a given substrate. Changing the number of surface amine groups in these systems inherently changes the surface energy of the silicon substrate. Amine groups are more polar than the alkane groups present on the PTMO. Therefore, increasing the NH$_2$ group density will increase surface energy, thus reducing the water contact angle of the silicon wafer. Fig. 6 shows the empirical relationship between water contact angle and the percentage of APS comprising the silane in the treatment solution. A PTMO-based polysiloxane, which contains no amine groups, yields a contact angle of 85.3º ± 1.6º. An APS-based polysiloxane gives a contact angle of 67.5º ± 0.7º. From Fig. 6, it is clear that changing the receptor

4

group density decreases the overall water contact angle, thus increasing the surface energy of the silicon substrate.
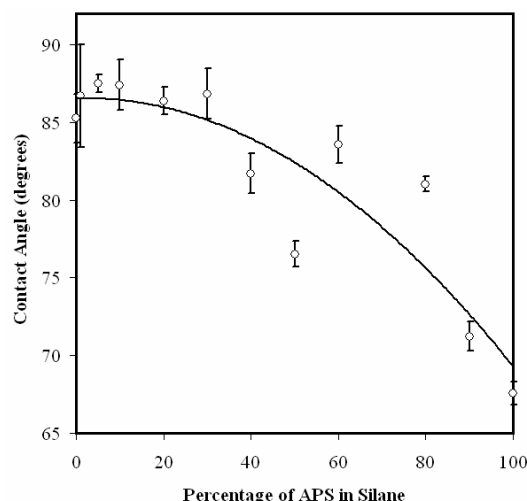

Fig 6. The relationship of water contact angle with the amount of APS contained in the silane during treatment.

3.3 Silica Deposition Methods

Two routes were utilized to deposit silica nanoparticles onto model silicon substrates. The first route relied on an epoxy-amine reaction to yield inverted, non-hydrolyzed silanes on the glass surface, as shown in Fig. 7. In this technique, the amine receptor groups react with GPS silanes to produce several surface methoxy groups. RBS analysis of this surface before and after the GPS silane reaction shows only a very small shift in the energy of the silicon edge (Fig. 8), indicating that the GPS layer is no more than 2 nm thick. Next, the surface is exposed to an acidic (pH = 4.5) silica solution. When exposed, the surface undergoes simultaneous hydrolysis of the methoxy groups and condensation of the silica.

The second deposition method involves pre-functionalizing the silica with epoxy groups. Fig. 9 gives a schematic representation of this deposition route. First, a GPS silane undergoes a condensation reaction with hydroxyl groups on the silica to the surface. The next step involves exposing the aminated silicon surface to the epoxy-functional silica. An epoxy-amine reaction occurs that covalently bonds the silica to the glass surface.
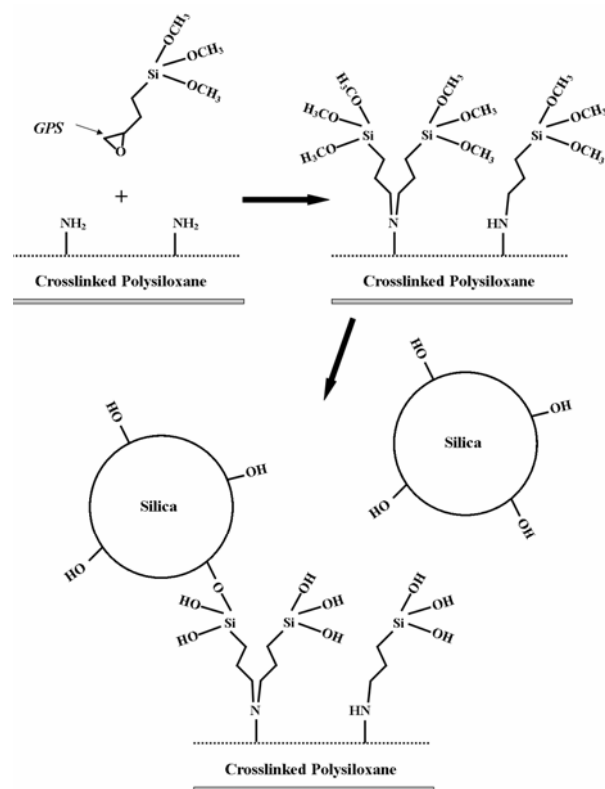

Fig 7. – One silica deposition route requires an epoxy-amine reaction with a GPS silane to yield a surface with methoxy groups. Silica is condensed to the silicon wafer surface after hydrolysis of the methoxy groups.
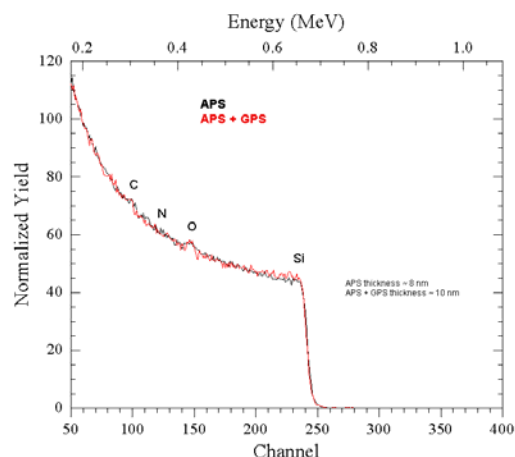

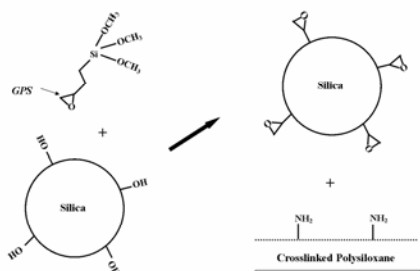**Fig. 8**. A slight shift in the Si edge indicates the GPS-layer is roughly 2 nm thick.

Fig. 9. A second silica deposition route involves the epoxy-functionalization of the silica and direct reaction with an aminated silicon substrate.

The second deposition method can potentially offer benefits over the first method. In the first route, an extra surface treatment is required prior to silica deposition. The simultaneous hydrolysis of surface methoxy groups and silica condensation can result in very complicated kinetic behavior that would make controlled deposition difficult. Potential exists for the silica to self-condense and agglomerate during deposition. Conversely, the second route relies on an epoxy-amine reaction for silica deposition. Therefore, only on silica particle and react at one amine site.

3.4 Surface Coverage

The overall goal of this work is to control the assembly of silica on a model glass surface. Three parameters were selected to investigate these effects: silica concentration during treatment, the functionalization of the silica, and amine receptor density.

3.4.1 Silica Concentration

The concentration of silica particles in the treatment solution can influence deposition in several ways. As concentration decreases, the ratio of silica particles to receptor groups also decreases. Therefore, there is potential that there would not be enough silica particles to fully satiate the number of receptor groups. A second effect of silica content is the interaction between particles during condensation. When silica concentration decreases (for non-functionalized silica), the interaction of the particles during condensation also decreases. Therefore, the potential for particle agglomeration becomes reduced.

Fig. 10 gives FESEM images for several concentrations of epoxy-functionalized silica reacted to a fully aminated (100% APS percentage) silicon wafer. Fig. 11 shows the corresponding surface coverage as calculated by imaging software. At 0.01 wt.% silica, the particles are sparsely dispersed on the surface, very little to no agglomeration is present, and surface coverage of roughly 14% is achieved. When silica concentration is increased to 0.1 wt.%, surface coverage significantly increases to 34%. A maximum surface coverage of 42% was achieved at 0.5 wt.% silica. As silica concentration increased past 0.5 wt.%, agglomeration of the particles became more pronounced. Since agglomeration cannot occur during the epoxy-amine reaction, this behavior probably occurs during the functionalization of the silica. Since the particles are functionalized in an acidic environment, some condensation/agglomeration may occur. The likelihood of this occurring would increase as with increasing silica content during the functionalization process.
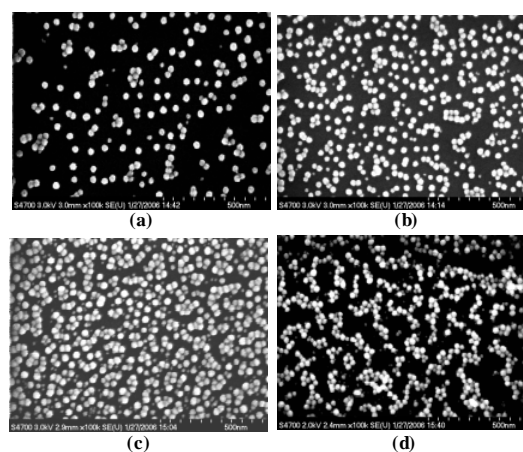

Fig. 10. FESEM images for epoxy-functional silica adsorption onto an APS-based polysiloxane (100%) in solutions containing (a) 0.01 wt.%, (b) 0.1 wt.%, (c) 0.5 wt.%, and (d) 1 wt.% silica.
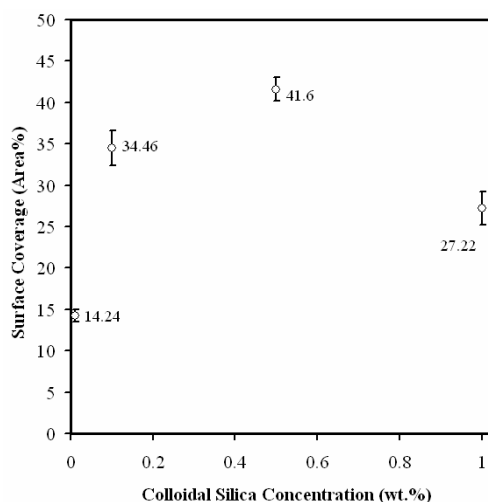

Fig. 11. Surface coverage of the surfaces given in Fig. 10 (calculated as described in Section 2.3).

6

Silica concentration also influences the adsorption of non-functionalized silica. Fig. 12 compares silicon wafers modified with 0.1 wt.% and 1 wt.% silica. At 0.1 wt.%, the surface coverage of particles is 51.3% ± 2.4%. At 1 wt.%, the silicon surface is fully covered with silica particles. For this sample, RBS was used to determine whether more than one layer of silica exists on the surface. Fig. 13 shows an RBS plot comparing the wafer surface before and after silica adsorption. The silica layer is calculated to be an average of 34 nm. Since the particles are 22 nm, this means that some of the surface has multiple layers of silica.
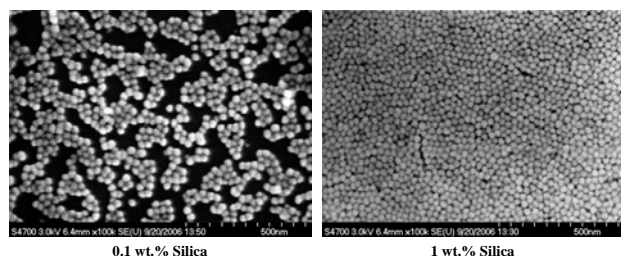

0.1 wt.% Silica   **1 wt.% Silica**

Fig. 12. FESEM images comparing a 0.1 wt.% (left) and 1 wt.% (right) non-functionalized silica treatment.
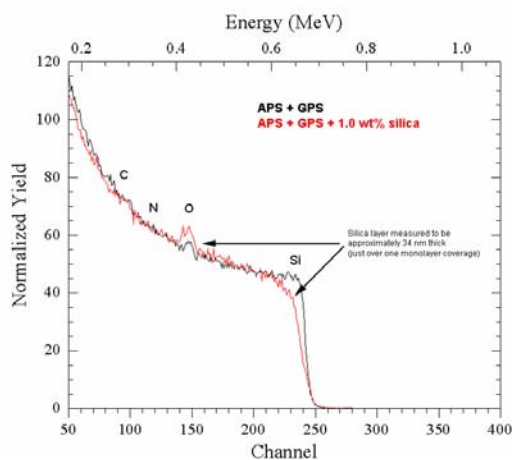

Fig. 13. RBS plot showing a shift in the Si edge that corresponds to an average silica layer thickness of 34 nm.

3.4.2   Silica Functionalization

Fig. 14 compares FESEM images of hydroxyl-functional (no modification) and epoxy-functional silica at 0.1 wt.% silica treatment on a 100% APS silane-treated silicon wafer. The surface coverage of the non-functionalized silica is roughly 51% as opposed to the 34% exhibited by the epoxy-functional silica. Additionally, the non-functionalized silica showed the much more agglomeration of the silica. Since the reaction is acid-catalyzed, condensation is likely to occur not only with the silicon surface, but with other silica

particles as well. Since epoxy-functional silica condenses through an epoxy-amine reaction, there are no possibilities of reactions between the particles.
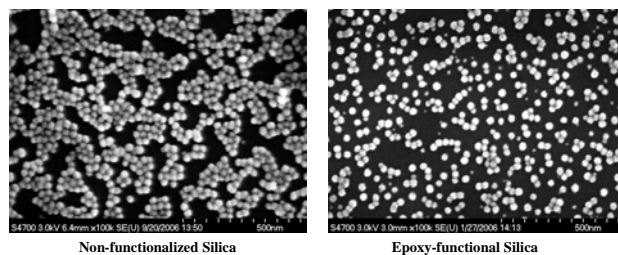

Non-functionalized Silica   **Epoxy-functional Silica**

Fig. 14. FESEM images comparing 0.1 wt.% treatments of non-functional (left) and epoxy-functional (right) silica.

3.4.3   Receptor Group Density

The density of amine groups on the wafer surface affects the number of potential reaction sites for silica bonding. Figure 15 gives FESEM images for a 10:90 APS:PTMO ratio surface and 100:0 APS:PTMO surface with 0.1 wt.% epoxy-functional silica treatment. In Figure 6, the atomic concentration of amine groups is 3.04 ± 0.2 mol % and 6.82 ± 0.83 mol %, respectively. There appears to be no real effect of amine density on the deposition of silica. It is probable that there is not a significant enough of a difference in amine density for one to see a large effect on surface coverage. Future work will investigate systems with even lower amine densities.
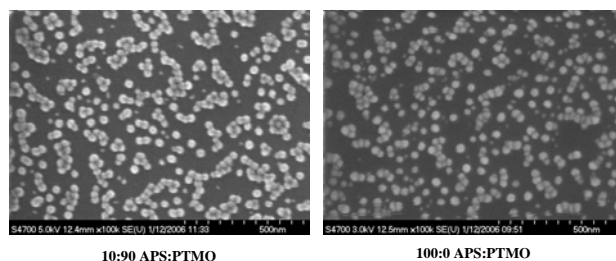

10:90 APS:PTMO   **100:0 APS:PTMO**

Fig. 15. FESEM images comparing 0.1 wt.% epoxy-functional silica treatments on surfaces corresponding to a 10:90 APS:PTMO and 100:0 APS:PTMO ratio formulation.

3.5 Surface Roughness

The surface coverage of silica has an effect on roughness. Fig. 16 shows how epoxy-functional silica concentration affect surface roughness values as obtained by the AFM. These data points correspond to the data contained Figs. 10 and 11. Fig. 17 shows the AFM profiles of each of these samples. As the silica particles become more dispersed on the silicon substrate, the roughness of the surface increases. This can be attributed to the ability of the tip to travel from the top of each silica particles to the silicon substrate. When the particles are

too closely packed, the AFM tip travels only a partial length of the particle diameter before contacting the neighboring silica particle. These results reinforce the idea that controlled silica deposition is required for increased nanotexturing of glass surfaces.
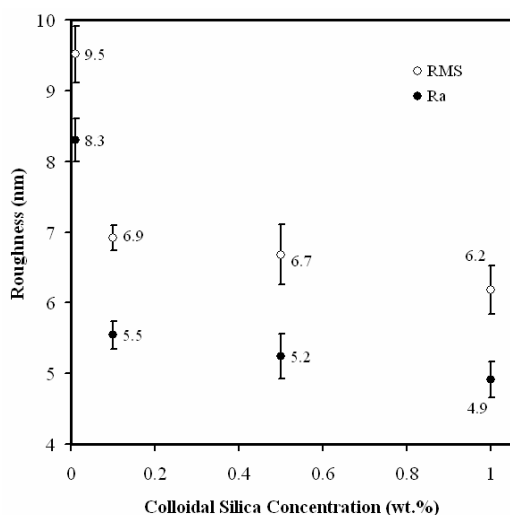

Fig. 16. RMS and Ra values for samples containing varying levels of silica surface coverage.
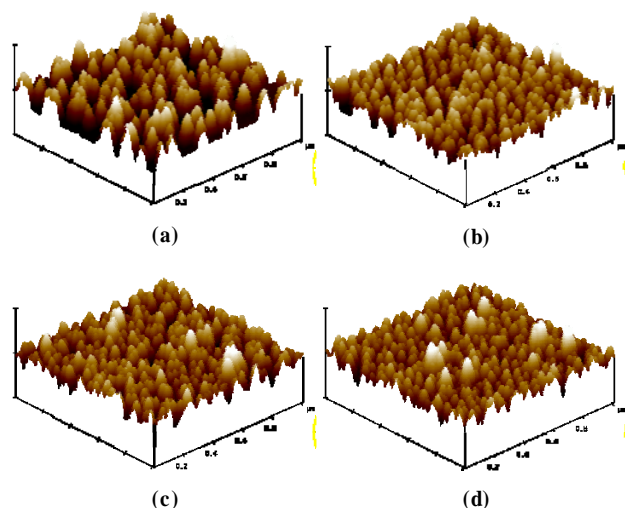

Fig. 17. AFM images for epoxy-functional silica adsorption onto an APS-based polysiloxane (100%) in solutions containing (a) 0.01 wt.%, (b) 0.1 wt.%, (c) 0.5 wt.%, and (d) 1 wt.% silica.

4. CONCLUSIONS

The overall goal of this paper was to determine which factors of silane/silica chemistry most influenced surface coverage and surface roughness of glass surfaces. Some general conclusions from this work are listed below.

- Typical silane formulations resulted in coupling agent layers roughly 8-10 nm thick.
- The number of amine receptor groups on the silicon surface can be controlled by varying the ratio of APS and PTMO silanes.
- Silica concentration in treatment solution affects surface coverage and overall particle agglomeration.
- Non-functionalized silica has more of an affinity for silica deposition and particle agglomeration than epoxy-functional silica.
- No noticeable differences in surface coverage are observed for surfaces with varying densities of amine receptor groups.
- Lower surface coverage of silica leads to rougher surfaces.

REFERENCES

Doolittle, L., 1986: A semiautomatic algorithm for Rutherford backscattering analysis, *Nuclear Instruments and Methods in Physics Research Section B*, **15**, 227-231.

Hirai Y., Hamada H., Kim J. 1998: Impact response of woven glass–fabric composites – I. Effect of fibre surface treatment, *Comp. Sci. and Tech.*, **58**,91–104.

Jensen, R. and McKnight S. 2006: Inorganic–organic fiber sizings for enhanced energy absorption in glass fiber-reinforced composites intended for structural applications, *Comp. Sci. and Tech.*, **66,** 509–521.

Plueddeman, E. 1991: Silane Coupling Agents, 2nd edn. Plenum Press, New York.